

Paramyosinogen, myosinogen, and myoglobin are proteids of the globulin class. They are all completely precipitated by saturation with magnesium sulphate, or sodium chloride, or by dialysing out the salts from their solutions. They can be separated by fractional heat coagulation, or by fractional saturation with neutral salts.

When muscle turns acid, as it does during *rigor mortis*, the pepsin which it contains is enabled to act, and at a suitable temperature (35—40° C.) albumoses and peptones are formed by a process of self-digestion. It is possible that the passing off of *rigor mortis*, which is apparently due to the reconversion of myosin into myosinogen, may be the first stage in the self-digestion of muscle.

XX. "Dispersion Equivalents. Part I." By J. H. GLADSTONE,  
Ph.D., F.R.S. Received May 24, 1887.

The idea of refraction equivalents has become familiar to those who work on the borderland of optics and chemistry, and the value of that property as a means of investigating the chemical structure of compounds is becoming more and more recognised. There is a similar property, perhaps equally valuable for the same object, which has attracted little attention hitherto; I allude to the equivalent of dispersion. During the last twelve months, however, I have collated old measurements of the length of the spectrum, whether made by myself or by others, and have added many new determinations, and I am now in a position to submit some of the results to the Society.

The history of the subject goes back to the first paper of Mr. Dale and myself upon the refraction of light,\* in which we gave as one of the conclusions "the length of the spectrum varies as the temperature increases." In our second paper† we came to the conclusion that "there is no simple relation holding good for different liquids between the increase of volume and the decrease of dispersion by heat," contrary to what we found to be the case with refraction. We adopted  $\mu_H - \mu_A$ , i.e., the difference between the refractive indices for the solar lines A and H as the measure of dispersion. This divided by the density gave the specific dispersion. When, however, Landolt adopted the plan of calculating the "refraction equivalent," we applied the same method to what we termed the dispersion equivalent, that is, "the difference between  $P\frac{\mu_A - 1}{d}$  and  $P\frac{\mu_H - 1}{d}$ , or more simply

\* "On the Influence of Temperature on the Refraction of Light." "Phil. Trans.", 1858, p. 8.

† "On the Refraction, Dispersion, and Sensitiveness of Liquids." "Phil. Trans.", 1863, p. 323.

$\frac{P^{\mu_H - \mu_A}}{d}$ ," where  $d$  equals the density of the substance and  $P$  its atomic weight.

In two communications made to the British Association,\* we stated that the dispersion equivalent of any substance is little affected by the manner in which it is combined with other bodies, and we gave as the mean value of  $\text{CH}_2$  0·35 in the vinic group, but higher figures in the benzene and pyridine groups; phosphorus equal to 2·9; chlorine 0·5; bromine 1·3; and iodine 2·6. In my subsequent paper in the 'Philosophical Transactions,'† in which the refraction equivalents of forty-six elements were worked out, I remarked, "the question of dispersion equivalents is also of interest; the data for the investigation of the matter are given in the Appendix." But there the matter rested. The paramount interest of the refraction equivalents in truth caused both the Continental observers and myself to neglect the question of dispersion; and with the exception of brief references to it in papers on Refraction,‡ nothing was published on the subject till last summer, when I applied the measurement of dispersion to the elucidation of the chemical structure of the essential oils;§ and afterwards in a paper at Geneva|| I ventured to give approximate values for fifteen elements.

Almost simultaneously with these appeared a paper by Brühl,¶ in which he endeavoured to eliminate the influence of dispersion from the refraction equivalents of highly refractive bodies. In this he seems to establish the fact that for such bodies at least, the theoretical formula of Lorenz,  $\frac{\mu^2 - 1}{(\mu^2 + 2)d}$ , gives more uniform results than the empirical formula  $\frac{\mu - 1}{d}$ ; but he draws as one of his conclusions, "the dispersion exercised by different bodies stands in no relation which is as yet clearly recognisable and measurable either with the refraction exerted by them, or with the chemical nature of the substances." In this and a following paper\*\* he gives additional proof of the worthlessness of Cauchy's dispersion formula, or any of the suggested modifications of it, to eliminate the influence of dispersion.

It will be seen that Brühl's conclusion is inconsistent with the views I have recently expressed, and the determinations I had already

\* 'Brit. Assoc. Rep.,' 1866. (Trans. Sec., pp. 10 and 37.)

† "On the Refraction Equivalents of the Elements." 'Phil. Trans.,' 1869, p. 27.

‡ 'Phil. Mag.' vol. 11, 1881, p. 59. 'Brit. Assoc. Rep.,' 1881 (Trans. Sec., p. 591). 'Chem. Soc. Journ.,' vol. 46, 1884, p. 258.

§ 'Chem. Soc. Journ.,' vol. 50, 1886, p. 609.

|| 'Archives Sci. Phys. Nat.,' vol. 16, 1886, p. 192.

¶ 'Liebig's Annalen,' vol. 235, 1886, p. 1.

\*\* 'Liebig's Annalen,' vol. 236, 1886, p. 233.

published; but while I am free to confess that there are many difficulties in the investigation of dispersion which have not been felt in dealing with refraction, I hold that the following conclusions are fully warranted by the data:—

1st. That dispersion, like refraction, is primarily a question of the atomic constitution of the body; the general rule being that the dispersion equivalent of a compound is the sum of the dispersion equivalents of its constituents.

2nd. That the dispersion of a compound, like its refraction, is modified by profound differences of constitution; such as changes of atomicity.

3rd. That the dispersion frequently reveals differences of constitution at present unrecognised by chemists, and not expressed by our formulæ.

In this paper my object will be to point out the uniformity that does exist, leaving apparent exceptions for future consideration.

Before entering upon an attempt to determine the dispersion equivalents of the different elementary substances, it may be well to consider the difficulty which occurred at the threshold of the enquiry, and another which appears to have deterred Brühl from prosecuting his enquiries in the direction of dispersion.

The original experiments of Mr. Dale and myself led to the belief that the "specific dispersion,  $\frac{\mu_H - \mu_A}{d}$ , slightly diminishes with increase of temperature"; but more accurate experiments made on the same specimens of bisulphide of carbon, benzene, brombenzene, and mint terpene, at the temperature of the observing room in the height of summer and depth of winter, have made me less confident of this conclusion. The variations are certainly within the limits of experimental error. The observations of Wüllner both upon bisulphide of carbon and water, those of Baille and v. d. Willigen upon water, as well as those of Pisati and Paternò on benzene and cymene, show that there is little, if any, appreciable difference in the specific dispersion at different temperatures. The general tendency of the observations on the seventy substances which have been examined more or less carefully, appears to be that the small difference of specific refraction that exists at different temperatures is a little greater in the case of H than in that of A.

Brühl gives three cases of isomeric or quasi-isomeric bodies. He measures the specific dispersion by the B of Cauchy's formula divided by the density. He shows that cinnamic alcohol,  $C_9H_{10}O$ , and cinnamic aldehyde,  $C_9H_8O$ , both of which he conceives to contain four pair of doubly-linked carbon-atoms, have a widely different specific dispersion; that allyl paracresolate and anethol,  $C_{12}H_{12}O$ , having four pair of doubly-linked carbon-atoms, are also quite different in

dispersion; and that, on the other hand, cymol and hexahydronaphthalin, both having the formula  $C_{10}H_{14}$ , but the first three pair, and the second two pair of doubly-linked carbon-atoms, have nearly the same dispersion. But if we reckon out the refraction equivalents for cinnamic aldehyde and for anethol from the numbers given in the same table, it will be seen that they are inconsistent with the supposition that these bodies have the chemical structure that he attributes to them; in fact the extremely high dispersion in each case only tells the same tale as the extremely high refraction. As to the two substances of the formula  $C_{10}H_{14}$  it is open to question whether hexahydronaphthalin has only two pair of doubly-linked carbon-atoms; and the refraction equivalent calculated for each of the specimens throws some doubt upon their purity. Brühl also compares methyldiphenylamine with cinnamic aldehyde, but the presence of nitrogen in the first body, and the uncertainty as to the constitution of the second, render it unsafe to draw any conclusions from the comparison. That the specific dispersion of isomeric or polymeric bodies is practically the same, except where the constitution is very different (as in aniline and picoline), was shown in my paper in the 'Philosophical Magazine' six years ago; and this must be set against the doubtful cases mentioned above.

#### *The Elements.*

There are but few of the elements of which the dispersive energy can be directly determined; but it so happens that two or three of these are among the most dispersive of bodies.

*Phosphorus* was determined by Mr. Dale and myself in a melted condition, and also by Damien both in that and the solid state. Our observation gives 3·1; those of Damien\* work out at 2·9 and 2·8 respectively.

*Sulphur*.—An old observation of mine on this body liquefied, gave 0·90 for E—A; and recent observations from its solutions in bisulphide of carbon give 1·2 for F—A. These agree in indicating about 2·6 for H—A.

*Selenium*.—According to the observations of Sirks,† the refractive indices for A and D are respectively 2·653 and 2·98; taking the specific gravity at 4·5, the dispersion equivalent of this element would be the extraordinary amount of 5·67 for D—A alone.

*Hydrogen*.—Ketteler's‡ observations give a dispersion equivalent of 0·0152 for the difference between the green line of thallium and the red line of lithium.

\* 'Journal de Physique,' 1881.

† 'Poggendorff, Annalen,' vol. 143, 1871, p. 429.

‡ 'Poggendorff, Annalen,' vol. 124, 1865, p. 390.

*Carbon*.—Schrauf's\* observations upon diamond give 0·058 for the dispersion equivalent of the same range.

*Iodine*, in the state of vapour, or dissolved in bisulphide of carbon, gives a spectrum in which the order of the colours is abnormal.

Far more important results have been obtained from organic substances, by following a method similar to that which Landolt adopted in his determination of the refraction equivalents of carbon, hydrogen, and oxygen. The materials for such an enquiry are very abundant. They consist of the observations published by Mr. Dale and myself in 1863, and my more recent determinations published and unpublished, the very valuable lists of Landolt and Brühl, numerous observations by Kanonnikoff, Nasini, and others. The Continental observers have usually adopted the lines  $\alpha$ ,  $\beta$ , and  $\gamma$  of the hydrogen spectrum.

On comparing the refraction equivalents of organic liquids of the fatty acid series which differ from one another by  $\text{CH}_2$ , or multiples of it, my best determinations lie between 0·33 and 0·36, averaging about 0·35 for each  $\text{CH}_2$ . On treating in a similar manner fifteen series of such bodies in Brühl's tables, some of which contain many terms, the dispersion equivalent for  $\gamma-\alpha$  works out very uniformly at an average of 0·215. This answers to 0·342 for H—A. Armstrong's cymhydrene, which is a saturated substance of the formula  $\text{C}_{10}\text{H}_{20}$ , has a dispersion equivalent of 3·44, giving therefore 0·344 for each  $\text{CH}_2$ . Kanonnikoff's determinations of tetraterpene and naphthene, also  $\text{C}_{10}\text{H}_{20}$ , give similar numbers. It may therefore be assumed that the value of  $\text{CH}_2$  in saturated organic compounds lies between 0·34 and 0·35, answering to the well known 7·6 as the refraction equivalent of the same combination. When, however, we examine unsaturated compounds in a similar manner, we find that the value rises to at least 0·40.

*Hydrogen*.—While the value of  $\text{CH}_2$  may be fairly taken at 0·34, it is more difficult to say what portion of this is due to the carbon, and what to the hydrogen. I have endeavoured to determine it, by deducting  $n$  times  $\text{CH}_2$  from the paraffines  $\text{C}_n\text{H}_{2n+2}$ ; by comparing the monatomic, diatomic, and triatomic alcohols, and by other similar means. The results are somewhat irregular, as might indeed be expected from the smallness of the residual figure, but give a mean of 0·04 per each hydrogen.

*Carbon*.—If the  $\text{H}_2$  in  $\text{CH}_2$  be taken at 0·08, it follows that the carbon will have a dispersion equivalent of about 0·26. This answers to the refraction equivalent of 5·0.

It is well known, especially from the researches of Brühl, that in unsaturated organic compounds, there is an increase of refraction, for

\* "Ueber das Dispersionsäquivalent von Diamant." "Wiedemann, Annalen," vol. 22, 1884, p. 424.

the line A, of about 2·2 for each pair of doubly-linked carbon-atoms. Assuming this to be due to a different value for carbon, we obtain a refraction equivalent of 5·0+1·1, i.e., 6·1. In all such cases there is a great increase of dispersion; this increase, however, is not always the same. In the allyl compounds, whether determined by Brühl, Kanonnikoff, or myself, it is uniformly very close to 0·5. In the olefines it is the same. In the whole of the aromatic series it is at least 0·8. Coincident therefore with the higher refraction equivalent for carbon, we have two dispersion equivalents of about 0·26+0·25, and 0·26+0·40, i.e., 0·51 and 0·66.

It must remain for future consideration, whether there may not be an intermediate refraction equivalent, corresponding to the dispersion equivalent of 0·51.

On the appearance of Brühl's papers in 1880, I ventured to suggest that there was a still higher refraction equivalent for carbon, in those cases in which it "has all four of its units of atomicity satisfied by other carbon-atoms, each of which has the higher value of 6·0 or 6·1," as in naphthalene or pyrene. This view has been, and is, the subject of controversy, but on turning to the dispersion equivalents of these bodies, they are found to be always enormously high, far higher than can be accounted for by the figures with which we have hitherto been dealing.

*Oxygen*.—It has been established by Brühl, that in the case of aldehydes and ketones, oxygen has a refraction equivalent of 3·4. As these have the general formula  $C_nH_{2n}O$ , and the dispersion of  $CH_2$  is known, it is very easy to determine the dispersion equivalent of the oxygen. Various determinations of these bodies give a fairly uniform result; viz., 0·18 for H—A.

In the case of the alcohols, the oxygen has a refraction equivalent of only 2·8. Comparing the dispersion equivalents of the alcohols of different atomicities in the published lists, the mean value for oxygen in this condition comes out at about 0·10. Nevertheless, in the organic acids and compound ethers, the value of the two oxygens together seems rarely if ever to exceed 0·24.

*Chlorine*.—Our lists also give us the means of determining the value of chlorine in organic substances of the fatty acid series. As reckoned from such substances as chloroform, chloral, ethylene, and ethylidene chloride, and bichloride of chlorethylene, the dispersion equivalent of this halogen appears to be 0·50, though in the simple chlorides of the compound radicles it appears to be a little less.

*Bromine*.—The dispersion equivalent of bromine varies in a similar way to that of chlorine. As deduced from bromoform and the dibromides of the olefines, it is 1·22; but in the bromide of ethyl it is lower.

*Iodine*.—The dispersion equivalent of iodine in di-iodide of me-

thylene was found to be 3·65, and in iodoform in solution it seems to be about the same; while in the ordinary iodides of the compound radicles it is much less.

*Nitrogen*.—Nitrogen appears to have a lower value in nitriles, cyanides, and sulphocyanides than in organic bases: but the figures obtained so far, for each condition of nitrogen, are not accordant. The lower value, however, probably does not exceed 0·10. The values of  $\text{NO}_2$  in the fatty acid series, as deduced from substitution products of the alcohols, glycerine, mannite, &c., are, however, fairly accordant, giving about 0·82.

*Sulphur*.—For the determination of sulphur, we have the excellent observations of Wiedemann,\* and Nasini;† the first on sulphur substitution products of carbonic ethers; the second on many organic compounds. There exist also two or three observations of my own. It appears that the value of sulphur in mercaptans, sulphocyanides, and sulphides of ethyl, butyl, amyl, and allyl, is about 1·21; answering to the refraction equivalent of 14·0.

But in bisulphide of carbon, where the refraction equivalent of sulphur is 16·0, the dispersion equivalent is 2·61: and this is about the value which the element appears to have in the isosulphocyanides, while the element itself dissolved in bisulphide of carbon, gives 1·20 for the dispersion F—A, which is equivalent to fully 2·5.

These results are collected together in the following table. The dispersion equivalents here given must however not be taken for anything more than approximate.

Substance.	Atomic Weight.	Refraction Equivalent A.	Dispersion Equivalent H—A.
Phosphorus .....	31	18·3	3·0
Sulphur, double bond .....	32	16·0	2·6
single bonds.....	"	14·0	1·2
Hydrogen .....	1	1·3	0·04
Carbon .....	12	5·0	0·26
" .....	"	6·1?	0·51
" .....	"	6·1	0·66
Oxygen, double bond .....	16	3·4	0·18
single bonds.....	"	2·8	0·10
Chlorine .....	35·5	9·9	0·50
Bromine .....	80	15·3	1·22
Iodine .....	127	24·5	3·65
Nitrogen.....	14	4·1	0·10
$\text{CH}_2$ .....	14	7·6	0·34
$\text{NO}_2$ .....	46	11·8	0·82

\* 'Journ. Prakt. Chem.', vol. 114, 1873, p. 453.

† 'Gazz. Chim. Ital.' vol. 13, p. 296.

It will be seen by a glance at this table, that the dispersion equivalents of the elementary substances are not in proportion to their atomic weights, or, in other words, that they have different specific dispersive energies. . Thus the analogous elements, sulphur and oxygen, are strongly contrasted in this respect, their specific refractive energies being respectively 0·081 and 0·011. Again it will be evident that the proportion between the refraction and dispersion is not the same even in the case of analogous elements. Thus, taking the three halogens, the ratio between the refraction for A and the dispersion for H—A for chlorine is about 100 to 5, for bromine 100 to 8, and for iodine 100 to 15.

*Metals in Salts.*—In 1869, as already stated, I suggested that the same data from which the refraction equivalents of the metals had been determined, would be available also for their dispersion equivalents. I have many observations in addition to the data then published; and Kanonnikoff has been over part of the same ground, measuring the  $\alpha$  and  $\beta$  of the hydrogen spectrum. Unfortunately, however, the errors of observation bear so considerable a proportion to the whole amount observed, at any rate in dilute solutions, that we cannot look upon single determinations of the dispersion equivalent of a salt as of much value. Thus, even when great care has been taken in measurement, each index of refraction is liable to an error of  $\pm 0\cdot0001$ , and as the error in determining A and H may be in opposite directions,  $\mu_H - \mu_A$  cannot be relied upon within  $\pm 0\cdot0002$ . Now among solutions of salts the specific dispersion rarely amounts to 0·02; the error of observation may therefore be more than 1 per cent., and if the salt should form only 5 per cent. of the solution, the error might exceed 20 per cent. Such solutions, therefore, are practically valueless for this purpose. Yet it would be easy to publish a table of miscellaneous salts, the dispersion equivalents of which had been deduced from several fairly accordant observations on fairly strong solutions, or which have been corroborated from some independent source. It has appeared preferable, however, to confine attention at present to the series of potassium and sodium salts, which are far the most complete and the most instructive.

It is evident at a glance, that the figures in the sodium columns are invariably lower than those in the potassium columns, and that the difference is fairly uniform. In regard to the refraction equivalent, it is about 3·33,\* and in the dispersion equivalent it is about 0·09.

It follows, that if we can determine the value of potassium, that of sodium may be at once calculated: and presumably the same process may be extended to all other metals that form soluble salts.

But it is not so easy to determine the value of potassium. In

\* Previously determined at 3·3.

	Refraction Equivalent.			Dispersion Equivalent.		
	Potassium.	Sodium.	Difference.	Potassium.	Sodium.	Difference.
Chloride ...	18·83	15·40	3·43	1·27	1·18	0·09
Bromide ...	25·25	21·80	3·45	2·17	2·08	0·09
Iodide ....	35·78	32·52	3·26	4·42	4·33	0·09
Hydrate ...	12·60	9·26	3·34	0·79	0·72	0·07
Formate ...	20·01	16·60	3·41	1·07	0·96	0·11
Acetate ...	27·52	24·34	3·18	1·32	1·23	0·09
Carbonate...	28·63	22·17	2(3·23)	1·40	1·34	2(0·03)
Oxalate....	37·55	..	..	2·18		
Nitrite ....	18·99	15·65	3·34	1·30*	1·17	0·13
Cyanide ...	17·18	..	..	0·94		

regard to the refraction equivalent, my original determination was 8·1; but Kanonnikoff gives only 7·75, which led me, three years ago, to recalculate the observations, taking Brühl's values for oxygen, and to reduce my previous estimate to 7·85. This is determined mainly from the organic salts, and the nitrate, and cyanide. I did not draw any conclusion from the haloid salts, as the chlorine, bromine, and iodine in them appear to have somewhat higher values than what they have in organic compounds.

How are we to determine the corresponding equivalent of dispersion? From the haloid salts it would seem to be about 0·8, but it seems likely that the disturbing influence, whatever it be, which increases the refraction of the haloid salts, would affect the dispersion. The formate and acetate,  $\text{KCHO}_2$  and  $\text{KC}_2\text{H}_3\text{O}_2$ , promise more trustworthy results, as we can subtract from their dispersion equivalents the numbers already determined for carbon, hydrogen, and oxygen. This will give respectively 0·53 and 0·44 for the dispersion equivalent of K.

If we view potassium hydrate,  $\text{KHO}$ , as water in which one hydrogen atom is replaced by potassium, water being 0·265, we obtain the value of 0·565 for K.

From the nitrite,  $\text{KNO}_2$ , by subtracting 0·82 for  $\text{NO}_2$ , we obtain 0·48 for K.

In like manner from the cyanide,  $\text{KCN}$ , by deducting 0·36 for cyanogen, we get 0·58 for K.

From the carbonate,  $\text{K}_2\text{CO}_3$ , by taking the probable value of the  $\text{CO}_3$  at 0·60, we get 0·40 for each K.

From the oxalate,  $\text{K}_2\text{C}_2\text{O}_4$ , by deducting 1·00 we get 0·59 for each K.

These figures, varying from 0·40 to 0·59, are too uncertain, and too

\* This is estimated from measurements of A, F, and G, and is somewhat open to doubt, as there seems to be something abnormal in the spectrum.

wide to give a good average. I doubt if such variations can be attributed wholly to experimental error; but on the other hand, it is difficult to imagine that potassium should have more than one dispersion equivalent, while in the same series of dissolved salts it has apparently one and the same refraction equivalent. I am more disposed to believe, that the uncertainty lies in the value of the radicles to which the metal is joined; but this will require a more extended research.

It is also an important enquiry:—To what extent does the modification of the dispersion equivalent affect the refraction equivalent for the line A? On this question, and others of a similar nature, I hope shortly to submit a further communication. I think it will be already sufficiently obvious that the specific dispersive energy of a compound body is a physical property analogous to, but distinct from, its specific refractive energy, and that it is capable in like manner of throwing light upon chemical structure.

**XXI. "On the Rate at which Electricity leaks through Liquids which are Bad Conductors of Electricity."** By J. J. THOMSON, M.A., F.R.S., Fellow of Trinity College, and Cavendish Professor of Experimental Physics in the University of Cambridge, and H. F. NEWALL, M.A., Assistant Demonstrator in Physics, Cambridge. Received May 26, 1887.

The experiments here described were undertaken to test whether the rate at which electricity leaks through a liquid which conducts electricity badly, does or does not follow Ohm's law.

The method used is described later on; it consists in establishing by a battery a difference of potential of about 100 volts between the plates of a condenser, in which the dielectric is the faulty insulator to be experimented on, then disconnecting the battery, and measuring with an electrometer the rate at which the difference of potential dies away.

Let  $v_1$  and  $v_2$  be the differences of potential at the beginning and end of an interval T, and let

$$\frac{v_1}{v_2} = x.$$

If  $c$  be the capacity of the condenser,  $q$  the quantity of electricity which has leaked away in the time T, then

$$v_1 - v_2 = \frac{q}{c};$$